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THE CHEMISTRY OF NITROGEN-CONTAINING HIGHER BORON HYDRIDE DERIVATIVES

FINAL REPORT

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Several synthetic studies of heteroborane cage compounds containing group 15 elements (N, P, As, Sb and Bi) have been completed. The synthesis of $B_9H_{11}NH$ from $B_{10}H_{14}$ has been improved. The first *closo* azaboranes, B_9H_9NH and $CpCo(NHB_9H_9)$ have been prepared and their properties investigated. The new phosphaborane derivatives $1,2\text{-}P_2B_{10}H_{10}$, $6\text{-(triethylamine)-}2\text{-}PB_9H_8$, $Na(B_{11}H_{11}P)$ and $2\text{-(triethylamine)-}1\text{-}PB_{11}H_{10}$ have been prepared and characterized. Several new metalloarsaboranes including $1,2\text{-}AsEB_{10}H_{10}$ (E = Sn and Pb) have been prepared and characterized. The first boron hydride cage molecules containing the element bismuth have been prepared. The compounds $1,2\text{-}Bi_2B_{10}H_{10}$ and $N(CH_3)_4[BiB_{11}H_{11}]$ are unusually stable to heat in the solid state.

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STATEMENT OF THE PROBLEM STUDIED

Initially, we studied the synthesis and chemistry of azaboranes. This class of compounds had been very little studied before our investigations. Subsequent studies have involved a more general investigation of group 15 (N, P, As, Sb, Bi) heteroborane chemistry.

A SUMMARY OF THE MOST IMPORTANT RESULTS

I. Azaborane Chemistry

We have done an extensive investigation of the reaction of $B_{10}H_{14}$ with sodium nitrite to form $Na[B_9H_{12}NH]$. This azaborane anion was oxidized with I_2 to form the very useful starting material, $B_9H_{11}NH$ in 57% yield (based on $B_{10}H_{14}$). The *nido*-$B_9H_{11}NH$ was converted to B_9H_9NH and $B_9H_9NH(CoCp)$, the first two *closo* azaboranes. Further chemical and ^{14}N NMR studies of the nitrogen unit in these *closo* azaboranes has been completed and published.

II. Phosphaborane Chemistry

Although arsaborane compounds are well known, the corresponding phosphaboranes have been little studied due to the complex nature of the reaction product mixture. The diphosphaborane, 1,2-$P_2B_{10}H_{10}$ has been prepared in low yield from $B_{10}H_{14}$ using PCl_3 as the source of phosphorus. This reaction gives several other products, one of which is 6-(triethylamine)-2-PB_9H_8, which has been fully characterized, including a single crystal X-ray structure determination. The thermal conversion of 1,2-$P_2B_{10}H_{10}$ to 1,7-$P_2B_{10}H_{10}$ occurred at 560-590 °C in a sealed tube. Aqueous base rapidly removed one phosphorus atom from 1,2-$P_2B_{10}H_{10}$ to form the 7-$PB_{10}H_{12}^-$ ion.

Treatment of $Na[B_{11}H_{14}]$ with triethylamine and PCl_3 formed both $Na[B_{11}H_{11}P]$ and 2-(triethylamine)-1-$PB_{11}H_{10}$.

III. Arsaborane Chemistry

Methods have been developed to improve the yield of 7-$AsB_{10}H_{12}^-$ and 1,2-$As_2B_{10}H_{10}$ to 50% based on $B_{10}H_{14}$. The icosahedral anion, $B_{11}H_{11}As^-$ has been obtained in 48% yield from $B_{11}H_{14}^-$. The metalloarsaboranes, 3,1,2-(dppe)Ni($As_2B_9H_9$), 3,6,1,2-$[(C_5H_5)Co]_2As_2B_8H_8$ and 1,2-$AsEB_{10}H_{10}^-$ (E = Sn and Pb) have been prepared and characterized.

IV. Bismaborane Chemistry

The first boron hydride structures containing the element bismuth have been prepared. The compound 1,2-$Bi_2B_{10}H_{10}$ was obtained in low yield from the reaction of $B_{10}H_{14}$ with triethylamine and $BiCl_3$. In the solid state, 1,2-$Bi_2B_{10}H_{10}$ starts to decompose at 350° and is surprisingly heat stable. Other bismaboranes that have been prepared and characterized are 1,2-$EBiB_{10}H_{10}$ (E = P, As and Sb) and $N(CH_3)_4[BiB_{11}H_{11}]$.

List of Publications

"Chemical and Structural Studies of Some Azaboranes", A. Arafat, J. Baer, J. C. Huffman, and L. J. Todd, *Inorg. Chem.*, **1986**, *25*, 3757.

"The Synthesis and Crystal Structure of $B_{10}H_{10}(C_6H_{11})S(CH_3)_2CNH(t\text{-}C_4H_9)$", D. M. Hernandez, J. C. Huffman, and L. J. Todd, *Inorg. Chem.*, **1987**, *26*, 213.

"The Synthesis of Polyhedral Arsaboranes and Their Metal Derivatives", T. P. Hanusa, N. R. Parisi, J. G. Kester, A. Arafat, and L. J. Todd, *Inorg. Chem.*, 1987, *26*, 4100.

"Further Synthetic Studies of $B_9H_{11}NH$. The Crystal Structure of $1(\eta^5\text{-}C_5H_5)\text{-}1,2\text{-}CoNHB_9H_9$", J. G. Kester, J. C. Huffman, and L. J. Todd, *Inorg. Chem.*, 1988, *27*, 4528.

"The Synthesis of Polyhedral Phosphaboranes. Crystal Structure of 6-triethylamine-2-PB_9H_8", J. L. Little, J. G. Kester, J. C. Huffman, and L. J. Todd, *Inorg. Chem.*, **1989**, *28*, 0000, in press.

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